

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO ELECTROLYTIC CELLS

(71) We, ROBERT BOSCH GMBH, a German Company, of Postfach 50, 7 Stuttgart 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electrolyte cells, especially fuel cells and relates in particular to a process for the production of gas-permeable hydrophobic sheets of polytetrafluoroethylene (PTFE) or other fluorine-containing polymers for such cells.

It is known that thin porous sheets of polytetrafluoroethylene can be produced by working polytetrafluoroethylene with a pore-former and suitable liquids into a paste which is rolled into sheets and then sintered.

The object of the present invention is to develop a process for the production of gas-permeable sheets which may be simple to carry out and in which the losses can be kept small; and which may produce sheets which are not permeable by the electrolyte even at relatively high hydrostatic pressure.

The present invention therefore provides a process for the production of a porous gas-permeable hydrophobic sheet of a fluorine-containing polymer, comprising electrophoretically depositing particles of one or more of said polymers from a suspension thereof onto a carrier electrode of the desired shape and sintering the deposited layer subsequent to the evaporation of the suspension medium.

If the layer is to be impermeable to electrolyte even at very high hydrostatic pressures ($p > 100$ cm water) it is rolled after being sintered.

It is also desirable in many cases to sinter the layer again after rolling especially if the hydrostatic pressures at which the layer is required to remain impermeable to the electro-

lyte are appreciably higher than 150 cm water; this naturally results in a lower gas permeability.

If PTFE is used, the sintering processes are carried out at temperatures between 330 and 400°C.

The suspending liquids used for electrophoretic deposition are preferably chloroform, carbon tetrachloride, trichloroethylene and water.

The present invention will be further described with reference to the following specific examples.

Example 1

200 g of PTFE powder were finely dispersed in 4 litres of carbon tetrachloride using a suspension stirrer. Two round carrier or supporting high-grade steel sheet electrodes of diameter 10 cm were immersed in this suspension. The electrodes were positioned opposite each other 5 cm apart. The interelectrode potential was 20 kv, and the deposition time was about five seconds. The suspension was gently stirred during the deposition. The anode with the deposit layer was, after evaporating off most of the carbontetrachloride (five minutes at room temperature) sintered in a hot-air chamber at 370°C for 45 minutes. The PTFE sheet, which had a thickness of about 150 μ m as a consequence of the chosen deposition time, was easily detached from the said electrode. This sheet was rolled at a pressure of about 100 kg/cm² in sheet rolls and then sintered again at 380°C for 30 minutes. The sheet remained impermeable to electrolyte over an experimental period lasting for five days when exposed to the hydrostatic pressure of 190 cm water produced by a 1.5 m height of 6N-KOH solution.

Example 2

100 g of PTFE powder were suspended in 4 litres of trichloroethylene. The anode used

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was a 2 mm thick, 100 cm² area, plate of ceramic material to the back of which was attached a metallic conductor. The potential between the electrodes, which were 5 cm apart, was about 10 kv, and the deposition time was again about five seconds. The ceramic plate and the deposited layer were sintered at 360°C for 30 minutes followed by chilling in cold water. In this way a very tough and flexible sheet was obtained which was then rolled at a roll pressure of about 100 kg/cm² in sheet rolls. The sheet obtained in this way remained impermeable to electrolyte over the whole experimental period of five days when exposed to the hydrostatic pressure of 170 cm water produced by a 1.2 m height of 4.5N-H₂SO₄ solution.

The process according to the invention makes it possible to produce in a simple manner, and practically without appreciable loss of raw materials, sheets of polytetrafluoroethylene or other fluorine-containing polymers which have a very uniform thickness whilst having a shape of any arbitrary form as determined by the carrier or supporting electrodes. The sheets show good flexibility and are mechanically very stable, porous and gas-permeable, but are impermeable to electrolyte. At an excess pressure of 0.5 atm the air permeability amounts to 80 ml cm⁻² min⁻¹, while the impermeability to electrolyte is maintained up to a hydraulic pressure of about 200 cm water. These properties are exactly those required for the so-called self-breathing gas-diffusion electrodes in fuel cells, and for

this reason, they find preferential use in this field.

WHAT WE CLAIM IS:—

1. A process for the production of a porous gas-permeable hydrophobic sheet of a fluorine-containing polymer, comprising electrophoretically depositing particles of one or more of said polymers from a suspension thereof onto a carrier electrode of the desired shape and sintering the deposited layer subsequent to the evaporation of the suspension medium.
2. A process as claimed in claim 1 in which the layer is rolled subsequent to said sintering.
3. A process as claimed in claim 2 in which the layer is sintered again subsequent to being rolled.
4. A process as claimed in any preceding claim in which the suspension medium is chloroform, carbon tetrachloride, trichloroethylene or water.
5. A process as claimed in any preceding claim in which the said fluorine-containing polymer is polytetrafluoroethylene.
6. A process as claimed in claim 5 in which the sintering is effected at a temperature of from 330° to 400°C.
7. A process as claimed in claim 1 substantially as hereinbefore described with reference to any one of the foregoing Examples.

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